Preface

Semiconductor ultra thin film structures are attracting a lot of interest due to their novel properties arising from quantum size effects on electronic and vibrational states In recent years Si and Ge based structures are being extensively investigated to realize new devices as they can be easily integrated with the well established Si based IC technologies The properties of these systems were found to strongly depend on their microstructure and interfaces and hence, the importance of its characterization has increased tremendously Among the techniques available for structure and interfaces characterisation, Raman spectroscopy has proven to be a very useful method

Compared to bulk, Raman spectra of ultra thin films exhibit unusual red shift and asymmetrical broadening as the phonons are confined Also real time Raman probing of thin film growth can provide more insight to understand the nature of growth

The growth of Si and Ge based structure suffers from the serious limitation of Ge segregation into the underlying Si, consequently smearing the interface sharpness Surfactant mediated growth (SMG) has proven to be very useful in suppressing the Ge segregation Raman spectroscopy can readily identify the intermixing of Si & Ge and infer about the interface from the Si-Ge vibrational modes which appears at 400 cm^{-1}

Raman investigation on phonon confinement effect in ultrathin films and SMG of Si and Ge are very limited This may be due to the following limitations

Conventional backscattering Raman investigations of ultrathin films and their interfaces suffer from two serious limitations (a) The intensity of the light scattered from ultrathin film(s) (and their interfaces intermixed to a few atomic layers) may be less than the detection limit (b) Lower penetration depth of the exciting visible light can prevent the investigation of deep buried layer interfaces These limitations have been over come to a great extent using an optical interference technique termed as Interference Enhanced Raman Spectroscopy (IERS) This is basically a multilayer absorption or anti-reflection structure, where, more amount of light is trapped in ultrathin layer(s) (as well as in interfaces) which is (are) to be investigated and kept well within the penetration depth of the laser.

The present thesis aims at the IERS investigation of phonon confinement effect on Raman line shape and position for ultra thin Ge films under both ex-situ and in-situ condition. It also includes the IERS investigation of growth and interfaces of polycrystalline Si and Ge when they are grown on each other at different temperatures with and without Sb as surfactant.

In the present work, IERS structure was constructed with Al as the first layer over the substrate to reflect the incident exciting radiation. The second layer is a transparent dielectric film (a-SiO_2) This conventionally used a-SiO_2 has been replaced by polycrystalline CeO_2 films as it enables the growth of c-Ge at relatively low substrate temperature. The other advantages of ceria is that the lattice parameter is 5.41 $\AA$ which is close to Si and the films deposited at ambient condition are found to be crystalline. Therefore, it can serve as a buffer layer for the growth of Ge and Si films.

In order to obtain maximum possible absorption in ultra thin layer, the required ceria film thickness has to be computed. The calculation requires the knowledge of the optical constants (n&K) of the films used. For Al, Pt, Ge and Si, the n&K of bulk have been used. The optical constants of ceria films are sensitive to the process parameter and since it also serves as a buffer layer, it is essential to know its structure. Therefore, optical and structural properties of ceria films were investigated. In the present work, films have been prepared by Ion Beam Sputter Deposition(IBSD) process as it provides a variety of potential advantages.

Ceria films have been deposited by reactive IBSD at oxygen partial pressures of PO_2 of 5×10^{-5} mbar 1×10^{-4} mbar and 1.5×10^{-4} mbar. At the optimal PO_2 of 1×10^{-4} mbar, films have been deposited with substrate temperature(T_s) being from ambient to 500°C. Ceria films deposited at ambient temperature with PO_2 of 1×10^{-4} mbar have shown refractive index of 2.36 which increased to 2.44 at T_s = 400°C. Raman spectroscopy and XRD have been used to characterise the structural properties. Raman line broadening, peak shift and XRD broadening indicate the formation of nanocrystalline phase for the films deposited up to 300°C However, crystallanity of the films deposited at $T_s >$ 300°C were much better In general, both structural and optical properties of reactive IBSD ceria films were unusual compared to the films deposited by conventional electron beam evaporation This has been attributed to (a)thermal effect (b)the bombardment of back scattered ions/neutrals from the target on the growing films and (c)the higher kinetic energy of the condensing species From the above detailed study, in order to construct IERS structure, ceria films have been deposited at ambient and 400°C for the investigation of phonon confinement and SMG, respectively

Having optimized the ceria deposition conditions, the following trilayer structures have been prepared to study the phonon confinement effect in ex-situ (A) 2 nm Ge/ 33 nm CeO_2 / Al (B) 4 nm Ge/ 26 nm CeO_2/Al (C) 7 nm Ge/16 5 nm CeO_2/Al (D) 10 nm Ge/10 nm CeO_2/Al The investigation revealed that, with a decrease of Ge film thickness, the Raman line exhibits an increase in red shift of the peak position and line width The latter can be quantitatively explained on the basis of phonon confinement in the growth direction Raman spectra of the 2 nm and 4 nm thick Ge films show shoulder at $\sim 280\ cm^{-1}$ which could be attributed to surface phonons The changes in the Raman shift as a function of thickness showed that the films were compressively strained up to a thickness of $\sim$ 7 nm beyond which the strain is released

The confined optical phonons and the growth of Ge also have been investigated under in-situ condition For in-situ Raman a vacuum system has been developed with thermal evaporation facility and attached with Raman spectrometer In-situ IERS has been carried out at 600°C in thickness steps of 0 5 nm up to a maximum of 4 nm A broad band like shoulder over the low frequency side of the Raman spectra is seen for 0 5 nm and 1 0 nm thick Ge films Also the observed red shift and broadening for these films were found to be higher than those calculated based on phonon confinement model This has been attributed to the signals from the surface of Ge films/cluster with disordered amorphous like structure having large fraction of three fold co-ordination

The variation of red shift and broadening for the films of thickness ≥ 1.5 nm have been quantitatively explained based on the phonon confinement model

For the investigation of Si and Ge growth and interfaces grown up to 600°C, Al cannot be used as a reflector, as it is not stable at high temperatures. Hence, it has been replaced with Pt which is found to be stable. We have selected a thickness structure of 3.5 nm Ge/3.5 nm Si/16 nm CeO_2/Pt/subst and 3.5 nm Si/3.5 nm Ge/16 nm CeO_2/Pt/subst. This choice of IERS structure is to obtain optimal low reflection.

Ge films grown on Si without surfactant have segregated in to the underlying Si and formed an alloy of Ge_xSi_{1-x} as indicated from Ge-Si mode. The variation of $\delta\omega$ (for Ge-Ge and Ge-Si) indicates the increase of composition x from 0.07 to 0.17 with the increase of growth temperature from 400°C to 600°C. However, use of Sb as surfactant has strongly suppressed the intermixing. Si films have been observed to crystallize at low substrate temperatures on Ge with the presence of predeposited Sb layer. Unlike the growth of Ge/Si, the intermixing in the growth of Si on Ge is observed to be negligible small. Interfaces for the case of Si/Ge with and without surfactant are observed to be same. In general, the surfactants have resulted in better crystalline growth of both Si and Ge when compared to that on bare Si and Ge surfaces.

Thus the modified IERS structure has been found to be very useful in probing ultra thin crystalline semiconductor films and their interfaces.